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⑳ *Process for producing new polyester resin.*

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## Description

The present invention relates to a process for producing a new polyester resin which has outstanding toughness, abrasion resistance, and flexibility.

Hereto, there are known several processes for the production of polyester resins. According to them, linear polyesters are produced by reacting a dicarboxylic acid with a diol having etherified diphenyl and non-linear polyesters are produced by reacting an etherified polyhydroxyl compound as a third component in addition to said two components; alternatively non-linear polyesters are produced by reacting polybasic (at least tribasic) carboxylic acid as a third component in addition to said two components.

The polyester resins produced by these processes have good performance to some extent, but they still have some disadvantages. For instance, the linear polyester resin is readily soluble in the unsaturated monomer but lacks toughness and abrasion resistance, and consequently it is not necessarily satisfactory in performance as a curing polyester resin. It may be used as a binder for the toner used in electrophotography, but cannot be used for a high-speed copying machine which employs a heat roller for fixation. If it is used for such a copying machine, it will cause off-set.

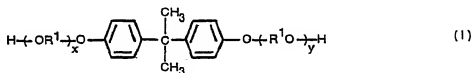
Non-linear polyesters, too, have a disadvantage. If an etherified polyhydroxyl compound is used as a third component, the resulting polyester resin improves in toughness and abrasion resistance, while maintaining to some extent the solubility in the unsaturated monomer. Nevertheless, it does not improve in glass transition temperature and tends to form a mass when used in the form of powder. On account of these disadvantages, the non-linear polyester cannot be used as a binder for glass fiber mat and as a binder for the toner used in electrophotography.

Moreover, the nonlinear polyester resin produced by reacting a polybasic (at least tribasic) carboxylic acid as a third component does not improve in properties if the acid is used in a small quantity. On the other hand, if the quantity of the acid is increased to produce a good effect, the resulting polyester resin becomes rigid and brittle and rises in softening point; in addition it is insoluble in the unsaturated monomer. Thus, such a polyester cannot be used as a curing polyester, and it tends to solidify in the reaction vessel during production. This invites a danger in the manufacturing process.

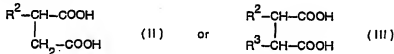
Under these circumstances, there has been a demand for a polyester resin which is outstanding in toughness and abrasion resistance and soluble in the unsaturated monomer and has a comparatively high glass transition temperature and an adequate softening point.

In order to overcome the above disadvantages, the present inventors have carried out a series of researches which led to the present invention.

The present invention relates to a process for producing a polyester resin by condensation polymerization of (a) a diol component represented by the formula:



(where R<sup>1</sup> is an alkylene group of 2 to 4 carbon atoms; and x and y are positive integers, the sum of them being 2 to 16 on an average), and (b) an acid component selected from the group consisting of polybasic (at least dibasic) carboxylic acid, anhydride thereof, and lower alkyl ester thereof, said process being characterized by that said acid component (b) contains 1 to 50 mol% of a dibasic carboxylic acid or anhydride thereof represented by the formula:



(where R<sup>2</sup> and R<sup>3</sup> are saturated or unsaturated hydrocarbon groups of 4 to 20 carbon atoms) and 10 to 30 mol% of trimellitic acid or anhydride thereof.

The more is used of the trimellitic acid or anhydride thereof, the higher is the glass transition temperature of the resulting resin and the more the abrasion resistance of the resulting resin is improved. This improvement is made at the sacrifice of increased rigidity. On the other hand, the more is used of the compound or anhydride thereof represented by the formula (II) or (III), the more the resulting resin is improved in impact resistance, flexing resistance, and solubility. This improvement is made at the sacrifice of the lowered glass transition temperature and the tendency that the powder of the resin tends to form a mass. These merits and demerits can be balanced if the quantity of the trimellitic acid or anhydride thereof is limited to 10 to 30 mol%, preferably 20 to 30 mol%, in the acid component (b), and the quantity of the compound or anhydride thereof represented by the formula (II) or (III) is limited to 1 to 50 mol% in the acid component (b).

Examples of acid component (b) other than (II) and (III) include phthalic acid, isophthalic acid, terephthalic acid, fumaric acid, maleic acid, anhydrides thereof, and lower alkyl esters thereof, which are used for the production of polyesters according to the present invention.

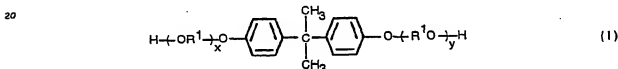
The polyester resin produced according to the process of this invention will be used (1) in the form of powder, (2) in the form of a solution dissolved in an organic solvent, and (3) in the form of a solution dissolved in an unsaturated monomer. For application of (3), it is necessary to use fumaric acid or maleic acid, which is an unsaturated dicarboxylic acid, as one of the acid components (b) other than (II) and (III); but for applications of (1) and (2), there is no limitation as to the kind of the acid to be used.

The polyester resin produced according to the process of this invention has a softening point of 80 to 150°C, preferably 100 to 140°C, as measured by the ring and ball method.

The polyester resin produced according to the process of this invention will be used in the form of powder as a binder for glass fiber mat and a binder for electrophotography toner, and in the form of a solution dissolved in an organic solvent as a binder to bond a photoconductive substance to the substrate.

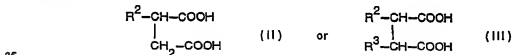
If an unsaturated dicarboxylic acid or anhydride thereof is used as one of the acid components (b), the polyester of this invention will be used as a so-called thermosetting polyester resin after being dissolved in an unsaturated monomer such as styrene, vinyltoluene, chlorostyrene, or diallylphthalate.

Examples of the diol which is used in this invention and is represented by the formula:



(where R<sup>1</sup>, x, and y are as defined above) include polyoxypropylene(2,2)-2,2-bis(4-hydroxyphenyl)propane, polyoxyethylene(2,2)-2,2-bis(4-hydroxyphenyl)propane, polyoxypropylene(6)-2,2-bis(4-hydroxyphenyl)propane, and polyoxypropylene(16)-2,2-bis(4-hydroxyphenyl)propane.

Examples of the dibasic carboxylic acid which is used in this invention and which is represented by the formula:



(where R<sup>2</sup> and R<sup>3</sup> are as defined above) include n-dodecenylsuccinic acid, iso-dodecenylsuccinic acid, n-dodecylsuccinic acid, iso-dodecylsuccinic acid, iso-octylsuccinic acid, and n-butylsuccinic acid.

The diol component used in this invention may be incorporated with less than about 5 mol % of a polyhydroxyl compound which is at least difunctional.

Examples of such polyhydroxyl compound include ethylene glycol, propylene glycol, glycerin, pentaerythritol, trimethylolpropane, hydrogenated bisphenol A, sorbitol, or etherified polyhydroxyl compound thereof such as polyoxyethylene(10) sorbitol, polyoxypropylene(3) glycerin, and polyoxyethylene(4) pentaerythritol.

According to the process of this invention, the polyester resin can be produced by polycondensing the polyol component and the polybasic carboxylic acid at 180 to 250°C in an inert gas atmosphere. In order to accelerate the reaction, a common esterification catalyst such as zinc oxide, stannous oxide, dibutyltin oxide, and dibutyltin dilaurate can be used. Also, the process can be carried out under a reduced pressure for accelerated reaction.

The invention will be illustrated by the following non-limitative examples for the production and use of the resin.

#### Production Example 1

Into a 1-liter 4-neck glass flask equipped with a thermometer, stainless steel stirrer, condenser, and nitrogen inlet were charged 700 g of polyoxypropylene(2,2)-2,2-bis(4-hydroxyphenyl)propane, 130 g of fumaric acid, 53.4 g of n-dodecenylsuccinic anhydride, and 0.1 g of hydroquinone. Using an electric mantle heater, the reactants were heated to 230°C, with stirring under a nitrogen stream, until the water formed by reaction was not distilled out any longer. The acid value at that time was 1.5.

Subsequently, 63.4 g of trimellitic anhydride was added and reaction was continued for about 8 hours until the acid value reached 20. A light yellow solid resin having a ring and ball softening point of 120°C was obtained.

#### Comparative Example 1

Into the same apparatus as used in Example 1 were charged 700 g of polyoxypropylene(2,2)-2,2-bis(4-hydroxyphenyl)propane, 333 g of fumaric acid, and 0.1 g of hydroquinone. Reaction was continued at 220°C

with stirring under a nitrogen stream, until the acid value reached 20. A light yellow solid resin having a ring and ball softening point of 108°C was obtained.

#### Comparative Example 2

Into the same apparatus as used in Example 1 were charged 700 g of polyoxypropylene(2,2)-2,2-bis(4-hydroxyphenyl)propane, 153 g of fumaric acid, and 0.1 g of hydroquinone. Reaction was continued until the water formed by reaction was not distilled out any longer. The acid value at that time was 1.8.

Subsequently, 63.4 g of trimellitic anhydride was added and reaction was continued for about 8 hours until the acid value reached 20. A light yellow solid resin having a ring and ball softening point of 125°C was obtained.

#### Usage Example 1

The resin obtained in Production Example 1 was incorporated with 65 wt% of styrene. The resulting clear polyester monomer solution was incorporated with benzoyl peroxide and then applied to a glass fiber mat. After curing at 90°C for about 1 hour, an inflexible glass fiber laminate was obtained.

On the other hand, the resin obtained in Comparative Example 1 was incorporated with 65 wt% of styrene. The resulting turbid solution was applied to a glass fiber mat in the same manner as above. The resulting glass fiber laminate caused whitening and cracking when bent.

The resin obtained in Comparative Example 2 was not dissolved in 65 wt% of styrene completely. Thus, the resulting solution was not suitable for production of glass fiber laminate.

#### Production Example 2

Using the same apparatus as used in Production Example 1, 650 g of polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane, 120 g of fumaric acid, and 53.4 g of iso-dodecenylsuccinic anhydride were reacted at 220°C, until the water formed by reaction was not distilled out any longer. The acid value at that time was 1.3.

Subsequently, 79 g of trimellitic anhydride was added and reaction was continued at 200°C until the ring and ball softening point reached 120°C. After standing for cooling and solidifying, the resin was crushed into powder which passes 42 mesh (350 µm opening) and contains more than 80% of the fraction which passes 42 mesh (350 µm opening) and remains on 150 mesh (100 µm opening).

#### Comparative Example 3

Using the same apparatus as used in Production Example 1, 617 g of polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane, 232 g of fumaric acid, and 9 g of glycerin were reacted at 220°C, until the ring and ball softening point reached 120°C. After standing for cooling and solidifying, the resin was crushed into powder which passes 42 mesh and contains more than 80% of the fraction which passes 42 mesh and remains on 150 mesh.

#### Usage Example 2

A glass fiber mat was produced as follows using as a binder the resin powder obtained in Production Example 2.

The first glass fiber layer was prepared by spreading uniformly chopped glass strand on a perforated steel plate measuring 35 cm by 35 cm placed in a mat producing test machine equipped with a blower. Water was sprayed for 10 seconds. With the blower stopped, the powder binder was spread uniformly on the mat. These steps were repeated four times to prepare a four-layered glass fiber mat. The mat was heated in an oven at 200°C for 10 minutes. The quantity of the powder binder was controlled so that the final loading is 3 to 4 wt% based on the glass fiber. On removal from the oven, the glass fiber mat was cooled immediately by putting between two steel plates. After cooling, the mat was cut to a size of 10 cm by 25 cm, and this test piece was measured for tensile strength on an autographic tensile tester (made by Shimadzu Selsakusho).

On the other hand, the powder binder was evaluated for caking by calculating the caking index as follows:

The resin powder prepared in Production Example 2 was vacuum dried at normal temperature for 2 days. Exactly 12 g of this powder was placed in a 40 cc beaker, and allowed to stand in the atmosphere of 55% RH and 40% RH, 70% RH and 100% RH for 2 days. The conditioned powder was kept pressed under a load of 200 g for 1 week. After removal of the load, the powder was taken out of the beaker slowly so as not to break the shape. The lump of the powder was dropped on a 20 mesh screen from a height of 50 cm. After slight shaking of the screen, the quantity of the powder remaining on the screen was measured. Let the weight W g, and the caking index is given by the following expression.

$$\text{Caking index} = W \times 100/12$$

The resin prepared in Comparative Example 3 and a commercial binder resin having the same particle size as that resin were evaluated for caking index, and the glass fiber mats produced from them were measured for tensile strength in the same manner as above. [The commercial binder resin is Atack 363E

(made by Kao Atlas), having an acid value 15 and a ring and ball softening point 112°C, made from polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane and fumaric acid. The results are shown in Table 1.

TABLE 1

	Mat tensile strength (kg)	Caking Index		
		35°C, 40% RH	35°C, 70% RH	35°C, 100% RH
10 Resin powder of Product Ex. 2	18.0	0	0	5
15 Resin powder of Comp. Ex. 3	15.5	0	55	85
20 Atlack 363E resin powder	15.0	0	45	75

Table 1 indicates that the resin powder obtained in Production Example 2 is superior in mat tensile strength and is more resistant to caking.

#### Production Example 3—1

25 Using the same apparatus as used in Production Example 1, 490 g of polyoxypropylene(2,2)-2,2-bis(4-hydroxyphenyl)propane, 195 g of polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane, 188 g of terephthalic acid, 26.8 g of *n*-dodecylsuccinic anhydride, and 0.8 g of diisopropyl orthotitanate as an esterification catalyst were reacted at 230°C for about 5 hours until the acid value reached 2.0.

30 Subsequently, 78.8 g of trimellitic anhydride was added and reaction was continued at 200°C for about 4 hours under reduced pressure until the ring and ball softening point reached 115°C. A light yellow solid resin having an acid value of 33 was obtained.

#### Production Example 3—2

35 In the same manner as Production Example 3—1, a resin having a softening point of 120°C was obtained. Those resins obtained in Production Examples 3—1 and 3—2 were soluble in organic solvents such as dioxane and methyl ethyl ketone.

#### Comparative Example 4—1

40 Using the same apparatus as used in Production Example 1, 490 g of polyoxypropylene(2,2)-2,2-bis(4-hydroxyphenyl)propane, 195 g of polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane, 204.3 g of terephthalic acid, and 0.8 g of diisopropyl orthotitanate were reacted at 230°C for about 5 hours. Subsequently, 78.8 g of trimellitic anhydride was added and reaction was continued at 200°C for about 4 hours under reduced pressure until the ring and ball softening point reached 115°C. A light yellow solid resin having an acid value of 34 was obtained.

#### Comparative Example 4—2

45 Comparative Example 4—1 was repeated except that the reaction was continued until the softening point reached 120°C.

#### Comparative Example 4—3

50 Comparative Example 4—1 was repeated except that the reaction was continued until the softening point reached 125°C.

#### Comparative Example 5—1

55 Using the same apparatus as used in Production Example 1, 490 g of polyoxyethylene(2,2)-2,2-bis(4-hydroxyphenyl)propane, 195 g of polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane, 97 g of terephthalic acid, and 0.8 g of diisopropyl orthotitanate were reacted at 230°C for about 5 hours. The acid value was 1.8. Subsequently, 156 g of trimellitic anhydride was added and reaction was continued at 200°C for about 5 hours until the ring and ball softening point reached 120°C. The resulting light yellow solid resin was insoluble in all the solvents tested, and it was very difficult to clean the reaction apparatus.

#### Comparative Example 5—2

60 Comparative Example 5—1 was repeated except that the reaction was continued until the softening point reached 125°C. The resulting light yellow solid resin was insoluble in all the solvents tested, and it was very difficult to clean the reaction apparatus.

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In both Comparative Examples 5—1 and 5—2, the polymerization rate was so high that there was a danger that the resin solidifies in the reaction apparatus.

## Usage Example 3

An electrophotography toner was prepared as follows. Ninety-five parts of the resin obtained in Production example 3—1 was mixed with 5 parts of carbon black in a ball mill, and then kneaded by a hot roll. After cooling and solidifying, the resin mixture was crushed by a hammer and then by a jet mill into fine powder having an average particle size of about 15 microns.

In the same manner as above, fine powders of the same particle size were prepared from the resins obtained in Production Example 3—2 and Comparative Examples 4—1 to 5—2.

Five grams each of the black fine powders was mixed with 95 g of iron powder of 150 to 200 mesh to make electrophotography toners. The toners were evaluated for the quality of images and off-set by applying by the magnetic brush method. The results are shown in Table 2.

TABLE 2

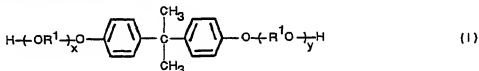
Resins	Ring and ball softening point (°C)	Off-set	Quality of image
Resin of Prod. Ex. 3—1	115	No	Good
Resin of Prod. Ex. 3—2	120	No	Good
Resin of Comp. Ex. 4—1	115	Yes	Blurred
Resin of Comp. Ex. 4—2	120	Yes	Good
Resin of Comp. Ex. 4—3	125	No	Poor fix
Resin of Comp. Ex. 5—1	120	Yes	Good
Resin of Comp. Ex. 5—2	125	No	Poor fix

Table 2 Indicates that the toners prepared from the resins obtained in Production Example 3—1 and 3—2 gave good images without causing off-set even in the case of the resin having a lower softening point.

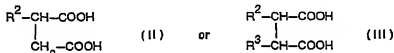
In contrast, the resins obtained in Comparative Examples 4—1 to 4—3 caused off-set except the resin having the highest softening point which is poor in fixation. This is also true in the case of the resins obtained in Comparative Examples 5—1 and 5—2. As mentioned above, these resins are more difficult to produce than the resin of this invention.

## Claims

1. A process for producing a new polyester resin by condensation polymerization of (a) a diol component represented by the formula:



(where R<sup>1</sup> is an alkylene group of 2 to 4 carbon atoms; and x and y are positive integers, the sum of them being 2 to 16 on an average), and (b) an acid component selected from the group consisting of polybasic (at least dibasic) carboxylic acid, anhydride thereof, and lower alkyl ester thereof, said process being characterized in that said acid component (b) contains 1 to 50 mol% of a dibasic carboxylic acid or anhydride thereof represented by the formula:



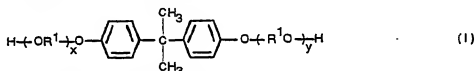
(where  $R^2$  and  $R^3$  are saturated or unsaturated hydrocarbon groups of 4 to 20 carbon atoms) and 10 to 30 mol% of trimellitic acid anhydride thereof, the balance 100 mol% being made up of other acid component(s) (b).

2. A process as claimed in Claim 1, wherein said dibasic carboxylic acid of the formula (II) or (III) is selected from the group consisting of n-dodecenylsuccinic acid, iso-dodecenylsuccinic acid, n-dodecylsuccinic acid, iso-dodecylsuccinic acid, iso-octylsuccinic acid, and n-butylsuccinic acid.

3. A process as claimed in Claim 1, wherein said condensation polymerization is conducted at 180 to 250°C in an inert gas atmosphere, in the presence of an esterification catalyst.

#### 10 Patentansprüche

1. Verfahren zur Herstellung eines neuen Polyesterharzes durch Kondensationspolymerisation von (a) einer Diolkomponente, repräsentiert durch die Formel



(wobei  $R^1$  eine Alkylgruppe mit 2 bis 4 Kohlenstoffatomen ist und x und y positive ganze Zahlen bedeuten, deren Summe im Durchschnitt zwischen 2 und 16 liegt) sowie (b) einer Säurekomponente, ausgewählt aus der Gruppe, bestehend aus mehrbasischer (mindestens zweibasischer) Karboxylsäure, deren Anhydrid und deren niedriger Alkylester, dadurch gekennzeichnet, daß die Säurekomponente (b) 1 bis 50 Mol% einer zweibasischen Karboxylsäure oder deren Anhydrid enthält, repräsentiert durch die Formel:



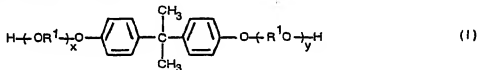
(darin bedeuten  $R^2$  und  $R^3$  gesättigte oder ungesättigte Kohlenwasserstoffgruppen mit 4 bis 20 Kohlenstoffatomen) und 10 bis 30 Mol% Trimellitsäure oder deren Anhydrid, wobei der Ausgleich zu 100 Mol% aus (einer) anderen Säurekomponente(n) besteht (b).

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die zweibasische Karboxylsäure der Formel (II) oder (III) ausgewählt ist aus der Gruppe, bestehend aus n-Dodecylsuccinsäure, Iso-Dodecylsuccinsäure, n-Dodecylsuccinsäure, Iso-Dodecylsuccinsäure, Iso-Octylsuccinsäure und n-Butylsuccinsäure.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Kondensationspolymerisation durchgeführt wird bei 180 bis 250°C in einer Atmosphäre aus inertem Gas, in der Anwesenheit eines Veresterungskatalysators.

#### Revendications

1. Procédé pour produire une nouvelle résine de polyester en polymérisant par condensation (a) un diol représenté par la formule:



(dans laquelle  $R^1$  est un groupe alkyle de 2 à 4 atomes de carbone; et x et y sont des nombres entiers positifs dont la somme est de 2 à 16 en moyenne), et (b) un constituant acide choisi parmi un polyacide (au moins diacide) carboxylique, un anhydride de celui-ci et un ester alkyle inférieur de celui-ci, ce procédé étant caractérisé en ce que le constituant acide (b) contient 1 à 50 moles % d'un diacide carboxylique ou d'un anhydride de celui-ci représenté par la formule:



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(dans laquelle R<sup>2</sup> et R<sup>3</sup> sont des groupes hydrocarb nés saturés ou insaturés de 4 à 20 atomes de carbone) et 10 à 30 moles % d'acide trimellitique ou d'anhydride de celui-ci, le complément à 100 moles % étant constitué d'un autre ou d'autres constituant(s) acide(s) (b).

2. Procédé selon la revendication 1, caractérisé en ce que le diacide carboxylique de la formule (II) ou  
5 (III) est choisi parmi l'acide n-dodécénysuccinique, l'acide iso-dodécénysuccinique, l'acide n-dodécylsuccinique, l'acide iso-dodécylsuccinique, l'acide iso-octylsuccinique et l'acide n-butylsuccinique.

3. Procédé selon la revendication 1, caractérisé en ce que la polymérisation par condensation se fait à  
une température comprise entre 180 et 250°C, en atmosphère de gaz inerte, en présence d'un catalyseur  
10 d'estérification.

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